



Stable nanoemulsions prepared via interfacial solidification of amphiphilic polyether–polyester block copolymers



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ABSTRACT

Oil-in-water (O/W) emulsions are generally stabilized by water-soluble surfactants, which anchor to the surface of oil droplets dispersed in an aqueous solution. Our recent work introduced a new approach to stabilize nanoemulsions through the formation of a semi-solid interphase at the O/W interface using a water-insoluble amphiphilic block copolymer, methoxy poly(ethylene glycol)-*block*-poly(ϵ -caprolactone). However, the approach is not applicable to relatively non-polar oils due to the quick precipitation of the hydrophobic PCL block within the oil phase. Here we report on successful stabilization of non-polar liquid paraffin nanoemulsions using an amphiphilic copolymers having a new hydrophobic block comprising ϵ -caprolactone and *L*-lactide. The new block copolymer was reorganized at the O/W interface of liquid paraffin, generating stable nano-sized emulsions via the formation of a robust semi-solid polymeric barrier. The prepared nanoemulsions show excellent dispersion stability even under a high level of mechanical stresses during freeze/thaw cycles.

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1. Introduction

Surfactants reduce interfacial energy between organic and aqueous phases, contributing to the stabilization of emulsions. Emulsion stabilization is controlled by multiple molecular interactions, including electrostatic interactions, steric hindrance, the Marangoni effect, and mechanical forces [1–3]. The distribution of small molecular weight surfactants in equilibrium is determined by the ratio of adsorption to desorption rates at the interface. Accordingly, a relatively large number of free surfactants are required to increase the number of surfactants bound to the surface of droplets, which is critically important in the stabilization of emulsions. However, it is desirable to avoid the use of a large amount of free surfactants particularly for biological applications because of their deleterious activities, including disintegration of biological membranes, protein denaturation, lipid extraction, and cytotoxicity [4–6].

Polymeric emulsifiers receive increasing attention as an alternative to small molecular weight surfactants because polymeric emulsifiers can have a much lower critical micelle concentration

(cmc), biological inertness, excellent chemical and structural stabilities, facile surface modification, and stimuli-responsive properties [7–13]. In general, the corona segments, which are exposed to the continuous phase, of polymeric emulsifiers have been widely studied because the steric hindrance has been known as a major mechanism of emulsion stabilization. The molecular conformation of a polymer chain at the interface has been also considered as an important factor for interfacial activities and structural stability. In particular, the penetration depth of a polymer chain into a dispersed droplet can greatly affect the stability of emulsions by reducing unfavorable interactions between an anchoring polymer chain and solvent molecules and constraining the conformation of a corona polymer chain to decrease its interaction with the dispersed phase [14,8,15,16]. Therefore, it has been generally accepted that, for successful stabilization of emulsions, the anchoring segment of a polymeric emulsifier needs to be highly soluble in the dispersed phase while the corona segment needs to be more extended toward the aqueous phase.

However, our recent study demonstrated that silicone oil-in-water emulsions can be effectively stabilized in the way completely contradictory to the concept described above [17]. As a polymeric emulsifier, we employed methoxy poly(ethylene glycol)-*b*-poly(ϵ -caprolactone) (mPEG-*b*-PCL), where PCL acts as a hydrophobic block that is insoluble in neither of the oil and aqueous phases, resulting in the solidification of the block copolymer at

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the O/W interface. Although mPEG-*b*-PCL was insoluble in commonly used oils at ambient temperatures, it was found that the block copolymer can be solubilized in ethanol around 60 °C, and the polymer solution was highly miscible with silicone oil at the same temperature. When the mixture of silicone oil and the polymer solution was dispersed in an aqueous solution, the block copolymers formed semi-solid, amphiphilic nanostructures at the interface, eventually stabilizing silicone oil-in-water emulsions [17]. In the following study on the preparation of nanoemulsions with mPEG-*b*-PCL, it was revealed that the type of oils (e.g., silicone oils, hydrocarbon oils, and ester oils) greatly affects the formation and dispersion stability of nanoemulsions [18]. Unfortunately, the applicability of mPEG-*b*-PCL as an emulsifier is limited to relatively polar oils, such as silicone oils and some ester oils. In contrast, nanoemulsions of non-polar oils (e.g., liquid paraffin (LP), dodecene, isopropyl myristate) were very unstable under various emulsification conditions. The materials properties and interactions involved in such differences remained unclear though the differences in the interactions of the PCL block with oils seem to be important in the conformation and distribution of the block copolymer at the O/W interface.

In this work, we investigated the impact of the hydrophobic block of amphiphilic block copolymers on the formation and dispersion stability of O/W nanoemulsions. A series of new amphiphilic block copolymers were synthesized by co-polymerization of ϵ -caprolactone (CL) and *L*-lactide (LL), forming a hydrophobic block, with mPEG as a hydrophilic block, resulting in methoxy poly(ethylene glycol)-*block*-poly(ϵ -caprolactone-co-*L*-lactide) (mPEG-*b*-PCLL). The biodegradability and biocompatibility of both of the hydrophobic components have been well established for biomedical and pharmaceutical applications [10,19,20]. This contribution particularly focused on PCLLs having relatively low weight ratios (0–12 wt.%) of LL to CL. Molecular weight, chemical compositions, and thermal properties of the synthesized block copolymers were determined, and the interfacial properties were investigated using silicone, ester, and hydrocarbon oils widely used in cosmetic and personal care products.

2. Experimental section

2.1. Materials

Methoxy poly(ethylene glycol) (mPEG, 5 kDa), CL, LL, tin(II) 2-ethylhexanoate (Sn(Oct)₂, 95%), dichloromethane (DCM), and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Dioctanoyl-decanoyl-glycerol (ODO), phenyl trimethicone (PTM), cethyl ethylhexanoate (CEH), and LP were obtained from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan).

2.2. Synthesis and characterization of mPEG-*b*-PCLL

Ring opening polymerization was performed to synthesize mPEG-*b*-PCLL. Briefly, calculated amounts of mPEG, CL, LL, and Sn(Oct)₂ were added to a 50 mL round bottom flask. The mixture was solidified in –25 °C for 10 min, evacuated at room temperature for 30 min, tightly sealed, and then heated to 120 °C to initiate polymerization. The mixture was magnetically stirred for 24 h. The weight ratio of monomers to mPEG was kept at 1.2, and that of monomers to Sn(Oct)₂ was 2000:1. The synthesized polymer was dissolved in dichloromethane and precipitated by pre-cold methanol (–25 °C) followed by centrifugation to collect the precipitates. This procedure was repeated three times to purify the product. Finally, the product was air dried at room temperature, milled into powders, and dried under vacuum for 24 h. ¹H nuclear magnetic resonance (NMR) spectrum was obtained at 25 °C with a Bruker

NMR operating at 300 MHz using CDCl₃ as a solvent. Chemical shifts were measured in parts per million (ppm) using tetramethylsilane as an internal reference. The molecular weight of the synthesized polymer was determined using gel permeation chromatography (GPC). A high performance liquid chromatography (HPLC) system composed of Agilent 110 series (Agilent Technologies, Palo Alto, CA, USA) and a refractive index detector was operated at 1.0 mL min⁻¹ using a series of three PLgel columns (300 × 7.5 mm, pore sizes = 10³, 10⁴, and 10⁵ Å) as size exclusion columns. Tetrahydrofuran was used as an isocratic mobile phase, and monodisperse polystyrenes (Polysciences, Inc., Warrington, PA, USA) were used as calibration standards. Thermal properties of the synthesized polymers were analyzed using differential scanning calorimetry (DSC 204 F1 Phoenix (Netzsch-Gerätebau GmbH, Selb, Germany). Two cycles of heating and cooling scans were run between –50 °C and 200 °C at a scan rate of 10 °C min⁻¹. Data from the second heating were analyzed, and the enthalpy of endothermic processes was determined.

2.3. Preparation and characterization of micelle-like aggregates of mPEG-*b*-PCLL

To prepare micelle-like polymer aggregates, 10 mg polymer powders were dissolved in 1 mL DMSO, and then the polymer solution was added to 10 mL deionized water with vigorous stirring. The prepared solution was dialyzed against an excess amount of deionized water at room temperature for 2 days. Micelle-like aggregates with different concentrations were prepared via serial dilution with deionized water to determine cmc as previously reported [21]. Two milligrams of pyrene were dissolved in 20 mL ethanol and diluted with deionized water to the final concentration of 4 × 10⁻⁴ mg mL⁻¹. Subsequently, 100 μL of a pyrene solution was added to 900 μL of mPEG-*b*-PCLL micelle-like aggregates. Fluorescence was measured with a fluorescence spectrophotometer F7000 (Hitachi, Japan) using a quartz cell. Fluorescence spectra were recorded from 350 nm to 450 nm with excitation at 332 nm. Scan speed was 240 nm min⁻¹, and the slit width was 5 nm for both of excitation and emission. The peak intensities at 372 nm and 383 nm were collected, and their ratios (I₃₇₂/I₃₈₃) were recorded as a function of the polymer concentration. The cmc values were calculated using a sigmoidal function (Boltzmann type) fitting curve. Size distribution of the micelle-like polymer aggregates was measured at 25 °C by dynamic laser light scattering (DLS) using a zeta-potential & particle size analyzer ELSZ-1000 (Otsuka Electronics Co., Ltd., Japan).

2.4. Wettability of mPEG-*b*-PCLL in Different Oils

One hundred milligrams of mPEG-*b*-PCLL was added into a vial contained 1 g of oils (ODO, PTM, CEH, and LP). The mixtures were kept at 80 °C for 24 h and then mixed vigorously by vortexing. The mixtures were cooled down to room temperature. Then, the separated oils were carefully taken out of the mixtures, and the weights of absorbed oils in the polymers were measured.

2.5. Preparation and characterization of O/W nanoemulsions

Ten milligrams of mPEG-*b*-PCLL and 100 mg of oil were dissolved completely in 1 mL of acetone using a bath-type ultrasonicator for 15 min. The solution was then dropped slowly into 10 mL of deionized water around 600 rpm at room temperature. The mixture was stirred at 40 °C for 24 h for complete evaporation of acetone. Size distribution of the prepared nanoemulsions was measured at 25 °C using DLS. To observe the prepared nanoemulsions by transmission electron microscope (TEM), 5 μL of nanoemulsion samples were mixed with 10 μL of 1% uranyl acetate

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